

Synthesis, characterization and unusual near-infrared luminescence of 1,1,4,4-tetracyanobutadiene derivatives

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1. General experimental procedures

Reagents were obtained from commercial suppliers and used without further purification. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer. Spectra were recorded in deuteriochloroform referenced to residual CHCl₃ (¹H, 7.26 ppm) or CDCl₃ (¹³C, 77.2 ppm). Chemical shifts (δ) are reported in ppm and coupling constants (J) are reported in Hz.

The following abbreviations are used to describe multiplicity; s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet. HRMS experiments were carried out on a Waters Q-ToF 2 (ESI-Electrospray Ionization, ASAP-Atmospheric Solids Analysis Probe) spectrometer. Analytical TLC was carried out on Merck 60 F₂₄₅ aluminium backed silica gel plates. Short wave UV radiation (245 nm), KMnO₄ and vanillin were used to visualize components. Compounds were purified by flash column chromatography using Geduran® silica gel 60 (0.040-0.063 nm).

Single crystal diffraction data were collected at low temperature on a D8 Venture Bruker AXS CMOS diffractometer with multilayers monochromatized Mo K α radiation. Structures were solved by dual-space algorithm using SHELXT program.¹ All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares techniques using the program SHELXL-2014.² Hydrogen atoms were located geometrically and treated using a riding model with isotropic atomic displacement parameter constrained to the equivalent adp of the bonded carbon atom. Powder X-ray diffraction data were obtained using a Bruker D8 Advance diffractometer working in the modified Bragg-Brentano geometry with a monochromatized Cu K α_1 radiation and equipped with a LynxEye fast detector. The analysis of the powder X-ray diffraction patterns was performed by Rietveld refinement using the FullProf³ and WinPLOTR⁴ packages. UV-visible spectra were recorded on a Jasco V-750 spectrophotometer using 1 cm² quartz cuvettes for solutions or a Jasco ISV-922 60 mm integrating sphere equipped with a micropowder sample cell (5 mm diameter \times 4 mm thickness) for solid samples. The luminescence spectra were measured using Horiba-Jobin-Yvon Fluorolog-3 spectrofluorometers. Powders were placed in quartz tubes inserted in a G8 GMP integrating sphere. The steady-state luminescence was excited with unpolarized light from a 450 W xenon CW lamp and detected at an angle of 90° with a Hamamatsu R928 photomultiplier tube (PMT), a Peltier cooled R2658 PMT or a liquid nitrogen-cooled InGaAs detector as specified. Long-pass filters with a 515-nm, 550-nm, 600-nm, 665-nm, 780-nm, or 850-nm cut-on wavelength were used to reject scattered light. Spectra were reference-corrected for both the excitation source light intensity variation (lamp and grating) and the emission spectral response (detector and grating).

The electrochemical measurements were performed with a conventional three-electrode

¹ G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8

² G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8

³ J. Rodriguez-Carvajal, *Physica B.*, 1993, **192**, 55–69.

⁴ T. Roisnel and J. Rodriguez-Carvajal, *Materials Science Forum*, 2001, **378**, 118–123.

system comprising a platinum electrode as the working electrode, a platinum wire as the auxiliary electrode and a saturated calomel electrode (SCE) as the reference electrode.

2. Syntheses

Synthesis of 1-(2,2-dibromovinyl)pyrene 4

A solution of aldehyde **3** (500 mg, 2.17 mmol) and CBr₄ (1.44 g, 4.34 mmol) in CH₂Cl₂ (8 mL) was treated at 0 °C with PPh₃ (1.77 g, 6.75 mmol) added portionwise over 10 min. The reaction mixture was stirred at 0 °C for 4 h 30. The reaction was quenched with H₂O (10 mL) and extracted with dichloromethane (3 x 20 mL). Organic layers were washed with H₂O (2 x 10 mL) and brine (10 mL), then dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 8:2) to give dibromoalkene **4** (578 mg, 1.49 mmol, 69%) as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.20 (m, 2H), 8.20 – 8.15 (m, 2H), 8.13 – 8.11 (m, 3H), 8.10 (s, 1H), 8.07 – 8.00 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 136.4, 131.4, 131.2, 130.8, 130.3, 128.3, 128.1, 128.0, 127.3, 126.4, 126.2, 125.7, 125.5, 124.7, 124.6, 124.5, 123.6, 93.2. HRMS (ASAP) calculated for C₁₈H₁₀⁷⁹Br₂[M⁺] m/z 383.9144, found: 383.9147

Synthesis of N,4-dimethyl-N-(pyren-1-ylethynyl)benzenesulfonamide 5

A solution of dibromoalkene **4** (565 mg, 1.46 mmol), TsNHMe (173 mg, 1.32 mmol), CuI (31 mg, 0.16 mmol), *N,N'*-dimethylethylenediamine (26 μL, 0.24 mmol) and Cs₂CO₃ (1.93 g, 5.29 mmol) in dry 1,4-dioxane (3 mL) was heated to 60 °C under a nitrogen atmosphere over 60 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 4:6) to give ynamide **5** (332 mg, 0.81 mmol, 61%) as a yellow/brown solid.

¹H NMR (400 MHz, CDCl₃) δ 8.46 (d, *J* = 9.0 Hz, 1H), 8.20 (ddd, *J* = 10.0, 7.7, 1.1 Hz, 2H), 8.13 (d, *J* = 9.2 Hz, 1H), 8.09 – 7.99 (m, 5H), 7.98 – 7.93 (m, 2H), 7.42 – 7.35 (m, 2H), 3.33 (s, 3H), 2.46 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 133.4, 131.6, 131.3, 131.1, 130.8, 129.9, 129.1, 128.2, 127.9, 127.9, 127.2, 126.2, 125.5, 125.5, 124.5, 124.4, 124.3, 117.4, 89.3, 68.6, 39.5, 21.7. HRMS (ESI, CH₃OH/CH₂Cl₂ 80/20) calculated for C₂₆H₁₉NO₂NaS [M+Na⁺] m/z 432.1029, found: 432.1028.

Synthesis of N,4-dimethyl-N-(1,1,4,4-tetracyano-3-(pyren-1-yl)buta-1,3-dien-2-yl)benzene sulfonamide 1

A solution of ynamide **5** (50 mg, 0.12 mmol) and TCNE (16 mg, 0.12 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 23 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to give TCBD **1** (41 mg, 0.08 mmol, 63%) as a purple solid.

¹H NMR (400 MHz, CDCl₃) δ 8.37 (dd, *J* = 8.5, 5.2 Hz, 3H), 8.34 – 8.27 (m, 2H), 8.19 – 8.09 (m, 4H), 7.77 – 7.69 (m, 2H), 7.42 – 7.36 (m, 2H), 3.08 (s, 3H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.0, 135.1, 132.3, 131.1, 131.1, 131.0, 130.8, 130.4, 130.0, 127.9, 127.7, 127.5, 127.2, 127.1, 125.1, 125.0, 124.1, 122.8, 112.1, 111.7, 111.0, 110.0, 93.8, 40.7, 21.8.

HRMS (ESI, CH₃OH/CH₂Cl₂ 80/20) calculated for C₃₂H₁₉N₅O₂NaS [M+Na⁺] *m/z* 560.1152, found: 560.1150 **Crystal data** (CCDC 1966903): C₃₂H₁₉N₅O₂S, *M* = 537.58 g.mol⁻¹, *T* = 150(2) K, monoclinic, space group = *P* 2₁/*n*, *a* = 8.7660(9) Å, *b* = 26.272(2) Å, *c* = 11.5682(9) Å, α = 90°, β = 109.987(3)°, γ = 90°, *V* = 2503.7(4) Å³, *Z* = 4, *D_c* = 1.426 g cm⁻³, absorption coefficient = 0.172 mm⁻¹, *F*(000) = 1112, reflections collected = 20815, independent reflections = 5619 (*R*_{int} = 0.0543), data/restraints/parameters = 5619/0/363. Final *R* indices (*I* > 2σ): *R*₁ = 0.0435. *R* indices (all data): *wR*₂ = 0.1069, goodness-of-fit on *F*² of 1.072.

Synthesis of 3-(2,2-dibromovinyl)perylene 7

A solution of aldehyde **8** (318 mg, 1.13 mmol) and CBr₄ (756 mg, 2.28 mmol) in CH₂Cl₂ (7 mL) was treated with PPh₃ (897 mg, 3.42 mmol) added portionwise over 10 min. The reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched with H₂O (20 mL) and extracted with dichloromethane (2 x 20 mL). Organic layers were washed with brine (20 mL), then dried over MgSO₄, filtered and concentrated in vacuum. The residue was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 3:7) to give dibromoalkene **7** (479 mg, 1.10 mmol, 97%) as a brown solid.

¹H NMR (400 MHz, CDCl₃) δ 8.24 – 8.09 (m, 4H), 7.81 (t, *J* = 0.7 Hz, 1H), 7.69 (m, 3H), 7.61 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 135.7, 134.6, 132.5, 132.0, 131.9, 131.7, 131.0, 130.8, 128.8, 128.4, 128.3, 128.1, 127.5, 127.0, 126.6, 126.6, 123.9, 120.7, 120.6, 120.6, 119.6, 92.9. HRMS (ASAP) calculated for C₂₂H₁₂⁷⁹Br₂ [M⁺] *m/z* 433.9300, found: 433.9302.

Synthesis of N,4-dimethyl-N-(perylene-3-ylethynyl)benzenesulfonamide 8

A solution of dibromoalkene **7** (260 mg, 0.60 mmol), TsNHMe (75 mg, 0.57 mmol), CuI (23 mg, 0.12 mmol), *N,N'*-dimethylethylenediamine (19 μ L, 0.18 mmol) and Cs₂CO₃ (718 mg, 2.20 mmol) in dry 1,4-dioxane (2 mL) was heated to 70 °C under a nitrogen atmosphere over 54 h. The reaction mixture was cooled to room temperature, diluted with ethyl acetate (10 mL) and filtered through Celite. The filtrate was concentrated under reduced pressure and purified by column chromatography (cyclohexane:dichloromethane 1:0 to 7:3) to give ynamide **8** (132 mg, 0.29 mmol, 50%) as an orange/brown solid.

¹H NMR (400 MHz, CDCl₃) δ 8.23 (ddd, *J* = 10.5, 7.7, 1.0 Hz, 2H), 8.17 (dd, *J* = 7.6, 1.0 Hz, 1H), 8.11 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.96 – 7.91 (m, 2H), 7.73 – 7.69 (m, 2H), 7.59 – 7.54 (m, 2H), 7.50 (td, *J* = 7.8, 4.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 3.30 (s, 3H), 2.49 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 134.5, 133.3, 131.0, 130.2, 129.9, 128.2, 128.0, 127.9, 127.2, 126.6, 126.6, 126.1, 120.7, 120.5, 119.8, 119.6, 89.6, 39.5, 21.7. HRMS (ESI, CH₃OH/CH₂Cl₂ 80/20) calculated for C₃₀H₂₁NO₂S [M⁺] *m/z* 459.1288, found: 459.1287.

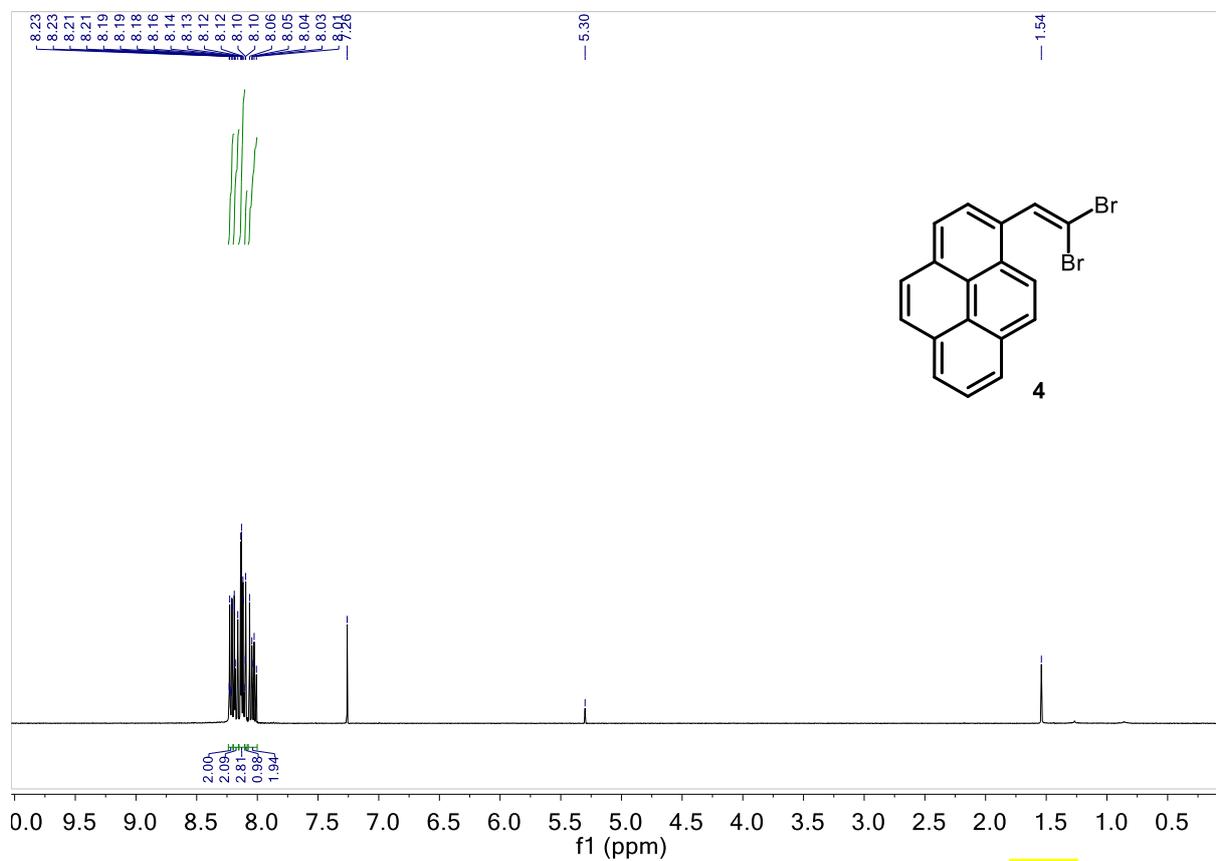
Synthesis of N,4-dimethyl-N-(1,1,4,4-tetracyano-3-(perylene-3-yl)buta-1,3-dien-2-yl)benzene sulfonamide 2

A solution of ynamide **8** (50 mg, 0.11 mmol) and TCNE (14 mg, 0.11 mmol) in CH₂Cl₂ (3 mL) was stirred at room temperature for 24 h. The reaction mixture was purified by column chromatography (cyclohexane:dichloromethane 1:0 to 0:1) to give TCBD **2** (46 mg, 0.08 mmol, 71%) as a green solid.

¹H NMR (400 MHz, CDCl₃) δ 8.37 – 8.22 (m, 4H), 7.80 (dd, *J* = 22.1, 8.0 Hz, 3H), 7.74 – 7.65 (m, 3H), 7.62 – 7.50 (m, 3H), 7.44 – 7.37 (m, 2H), 3.03 (s, 3H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 147.0, 137.8, 134.3, 132.9, 132.2, 131.9, 130.9, 130.6, 130.0, 129.3, 129.3, 129.2, 129.0, 128.0, 127.9, 127.0, 126.8, 123.2, 122.1, 121.7, 119.4, 112.1, 111.8, 111.2, 109.9, 92.9, 40.7, 21.8. HRMS (ESI, CH₃OH/CH₂Cl₂ 80/20) calculated for C₃₆H₂₁N₅O₂NaS [M+Na⁺] *m/z* 610.1308, found: 610.1306. **Crystal data** (CCDC 1966902): C₃₆H₂₁N₅O₂S, *M* = 587.64 g.mol⁻¹, *T* = 150(2) K, monoclinic, space group = *I* 2/*a*, *a* = 17.1162(16) Å, *b* = 7.7907(9) Å, *c* = 42.350(5) Å, α = 90°, β = 90.551(4)°, γ = 90°, *V* = 5647.0(11) Å³, *Z* = 8, *D*_c = 1.328 g cm⁻³, absorption coefficient = 0.159 mm⁻¹, *F*(000) = 2432, reflections collected = 24755, independent reflections = 6476 (*R*_{int} = 0.0367), data/restraints/parameters = 6476/0/397.

Final R indices ($I > 2\sigma$): R1 = 0.0442. R indices (all data): wR2 = 0.1230, goodness-of-fit on F^2 of 1.042.

3. ^1H NMR and ^{13}C NMR spectra



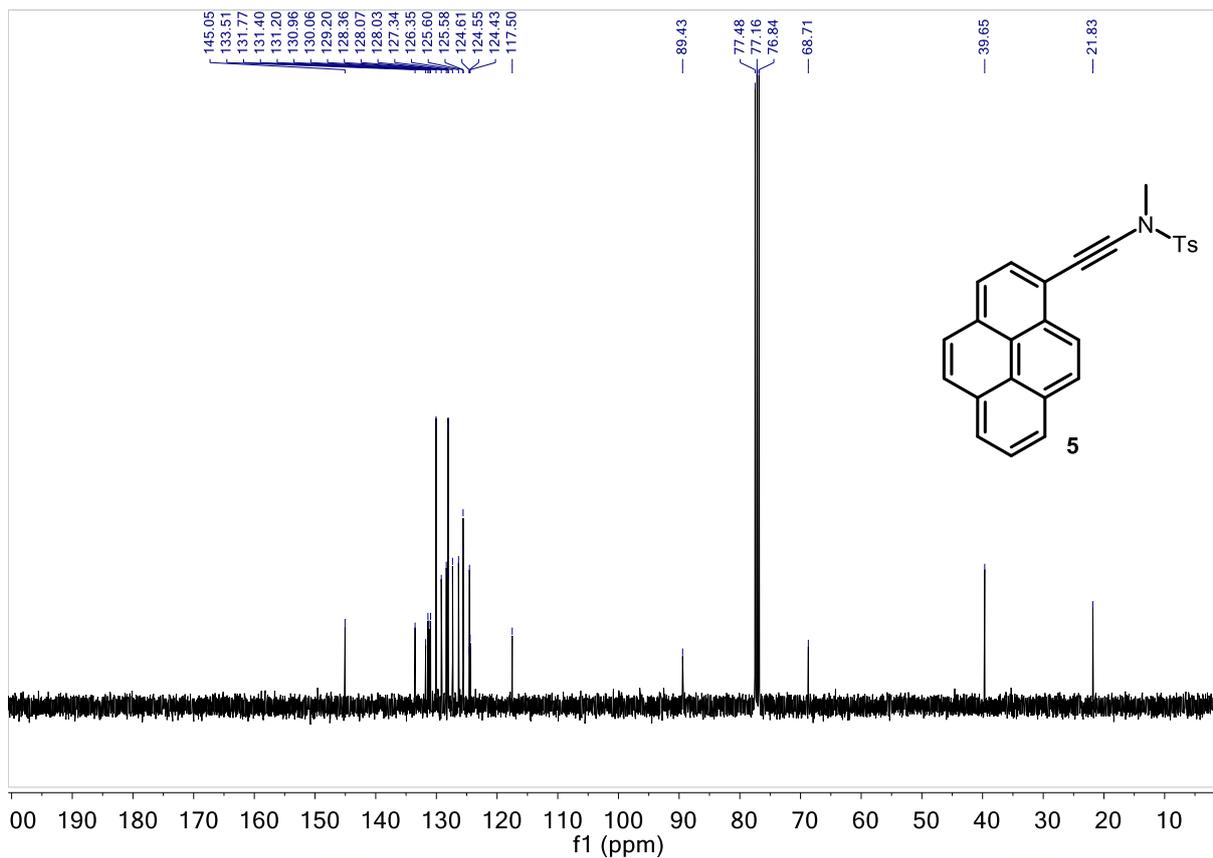


Figure S4. ^{13}C (75 MHz, CDCl_3) NMR spectrum of **5** recorded at 25°C .

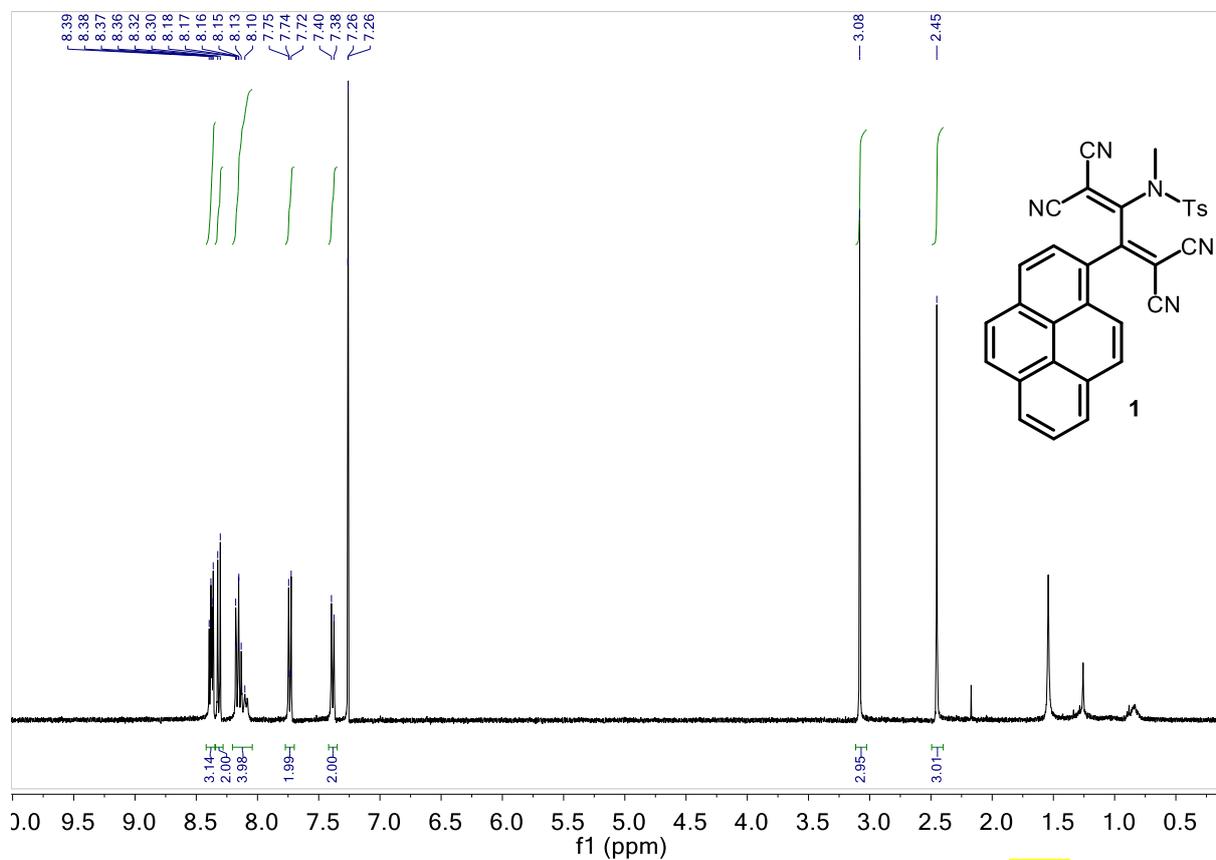


Figure S5. ^1H (300 MHz, CDCl_3) NMR spectrum of **1** recorded at 25°C .

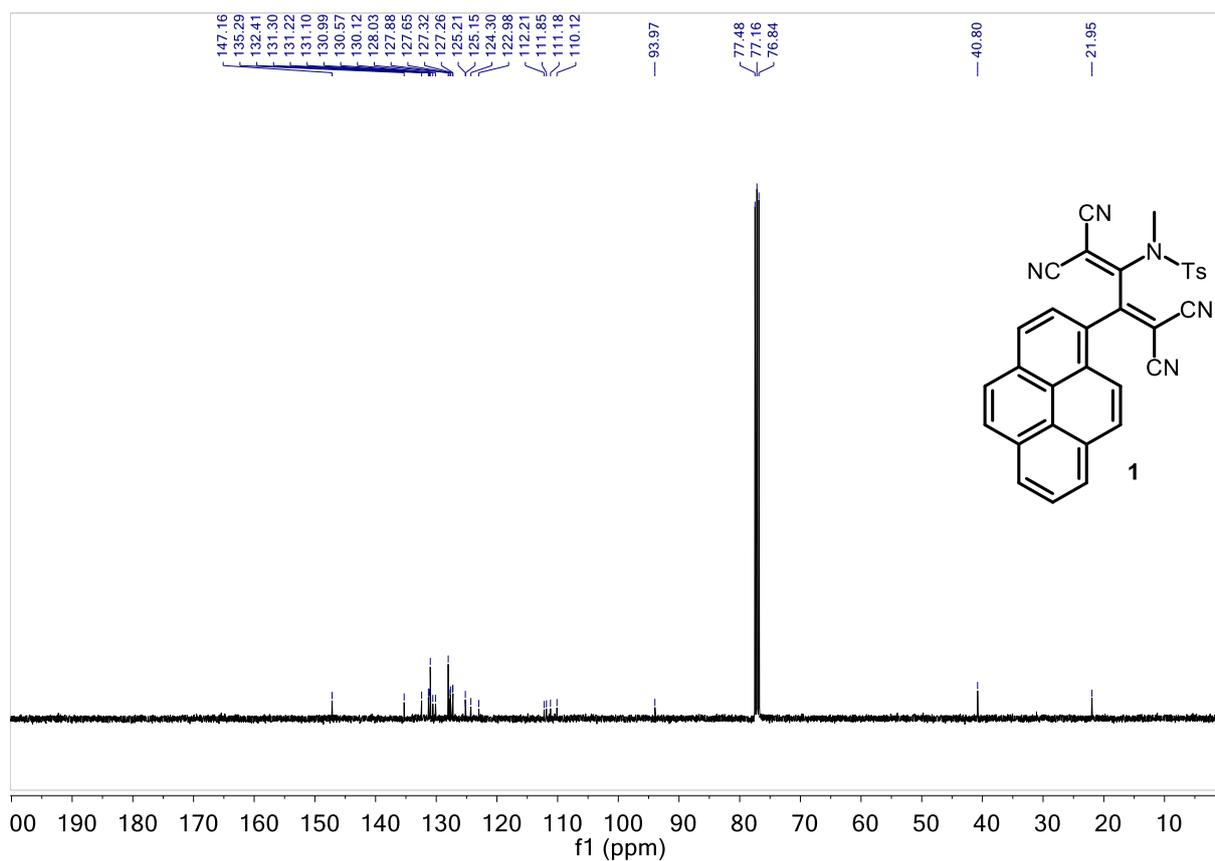


Figure S6. ^{13}C (75 MHz, CDCl_3) NMR spectrum of **1** recorded at 25°C .

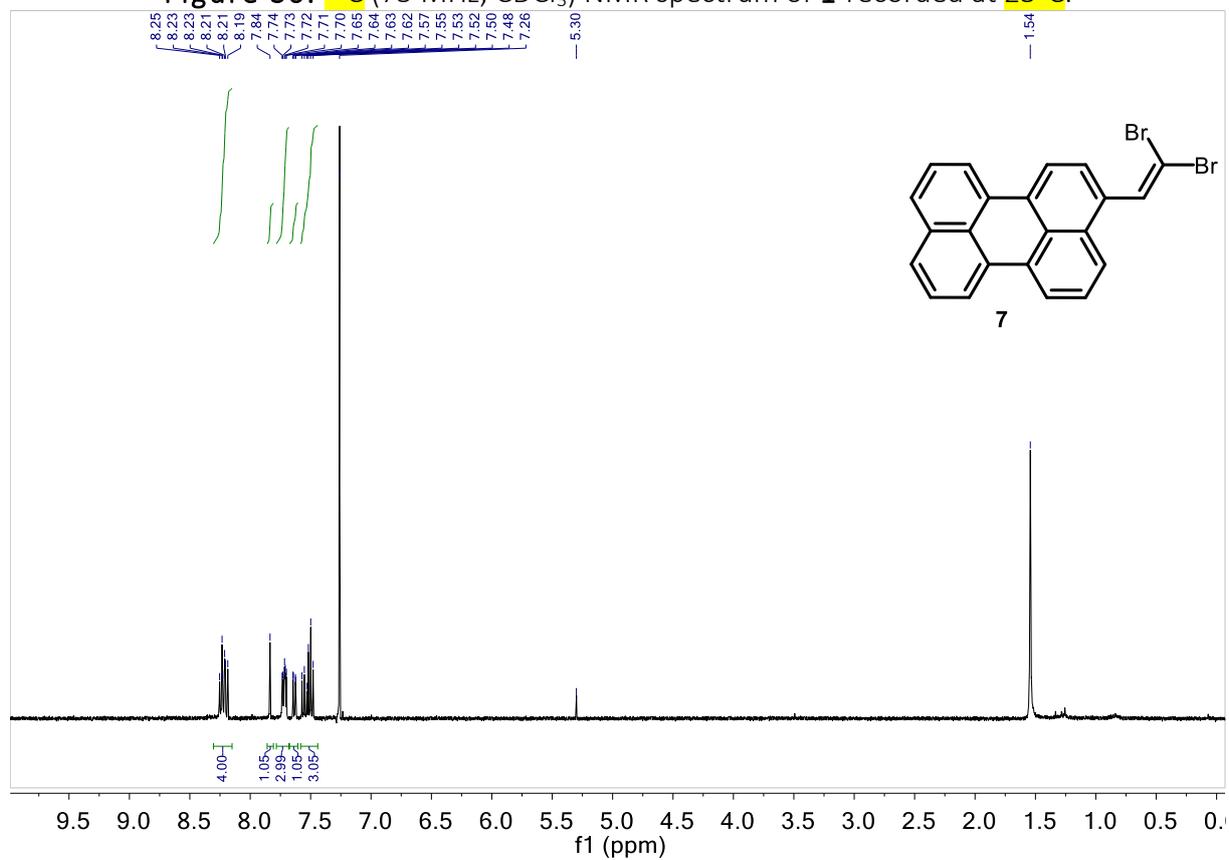


Figure S7. ^1H (300 MHz, CDCl_3) NMR spectrum of **7** recorded at 25°C .

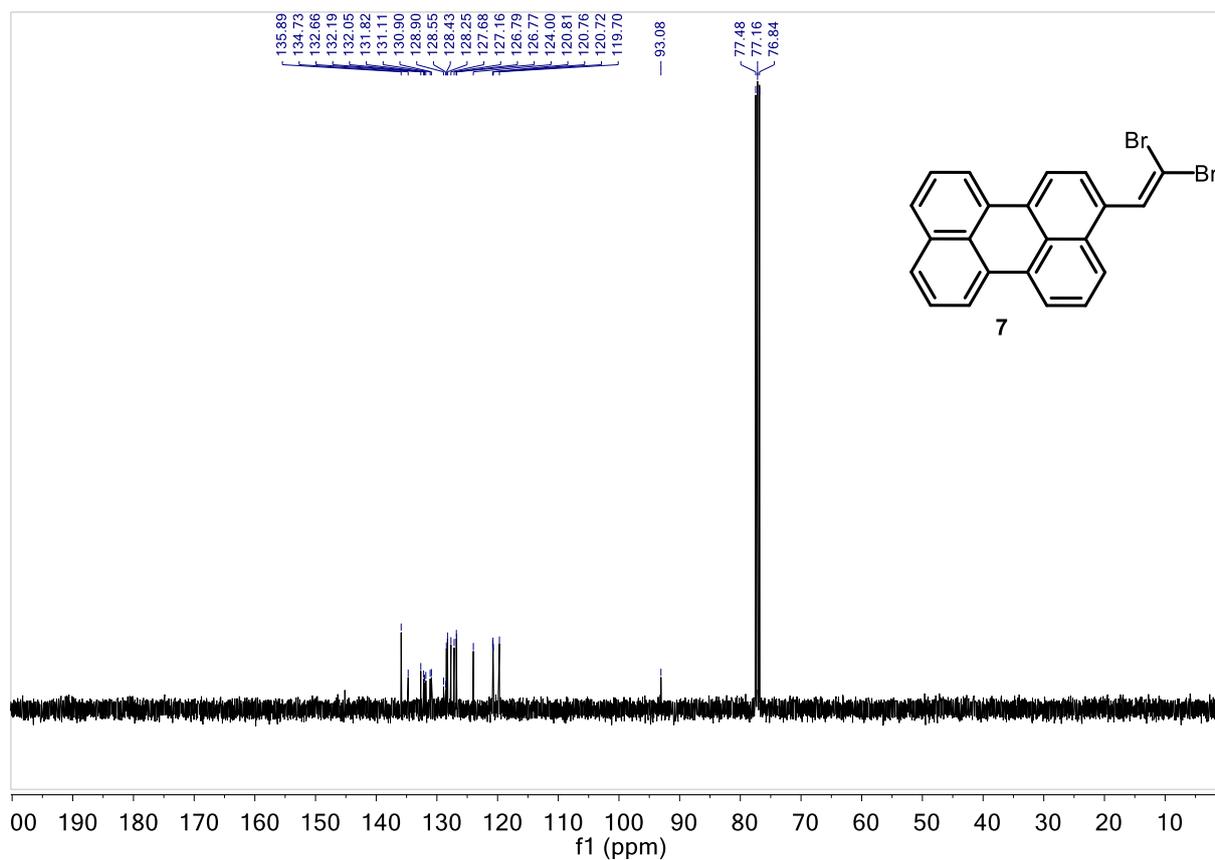


Figure S8. ^{13}C (75 MHz, CDCl_3) NMR spectrum of **7** recorded at 25°C .

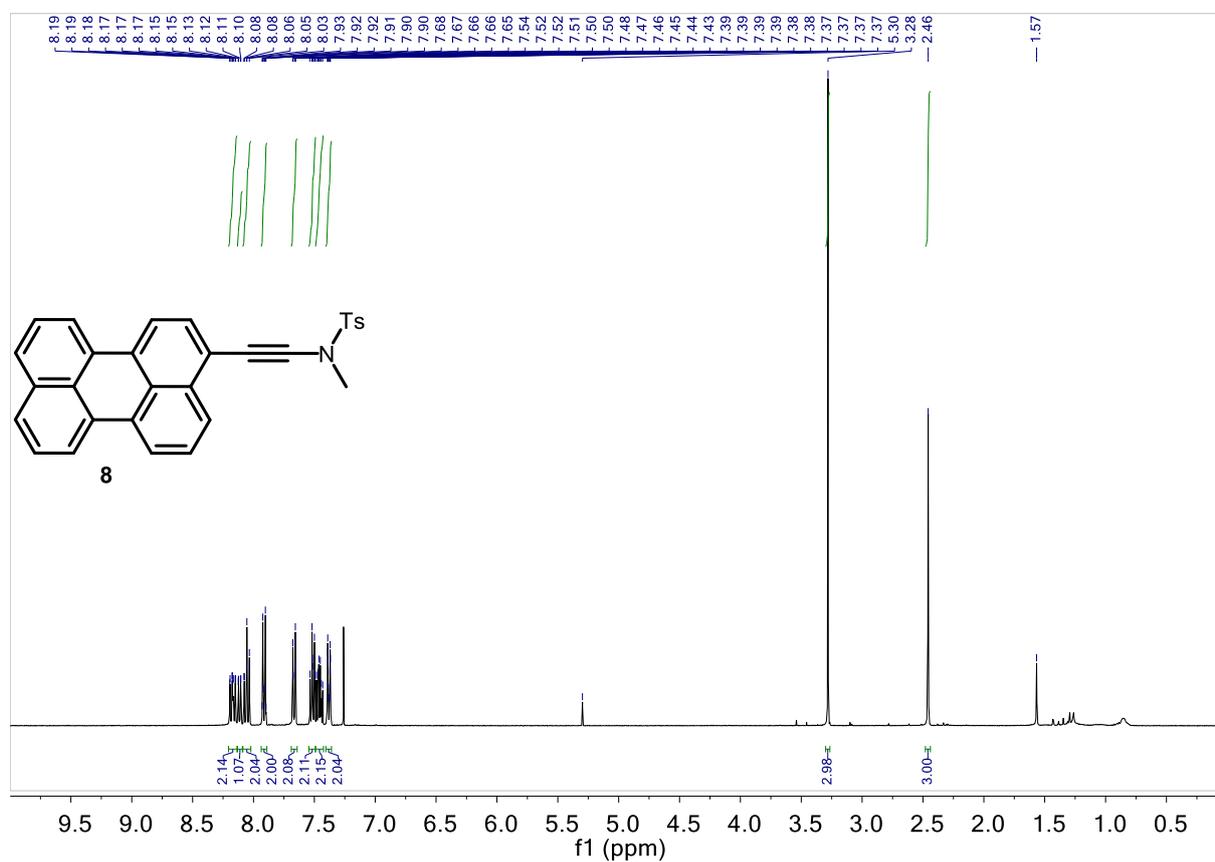


Figure S9. ^1H (300 MHz, CDCl_3) NMR spectrum of **8** recorded at 25°C .

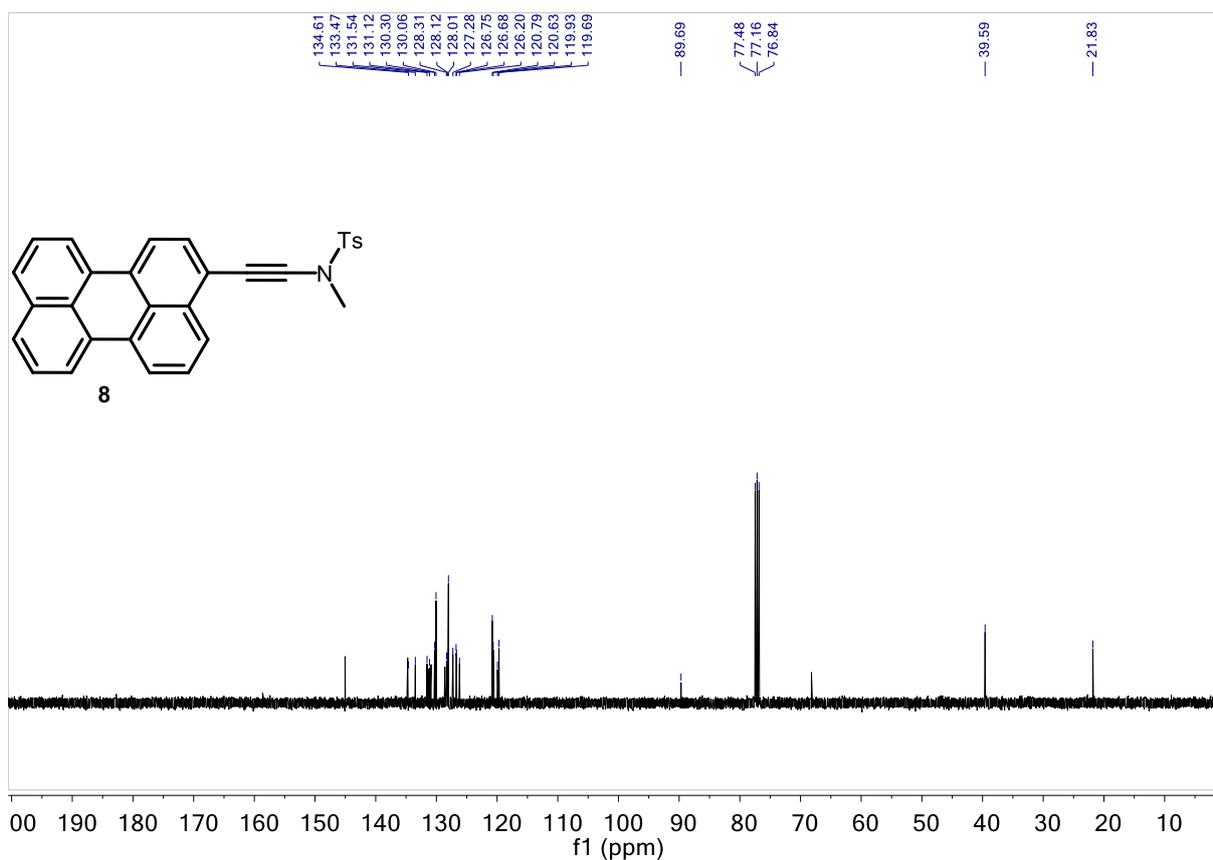


Figure S10. ^{13}C (75 MHz, CDCl_3) NMR spectrum of **8** recorded at 25°C .

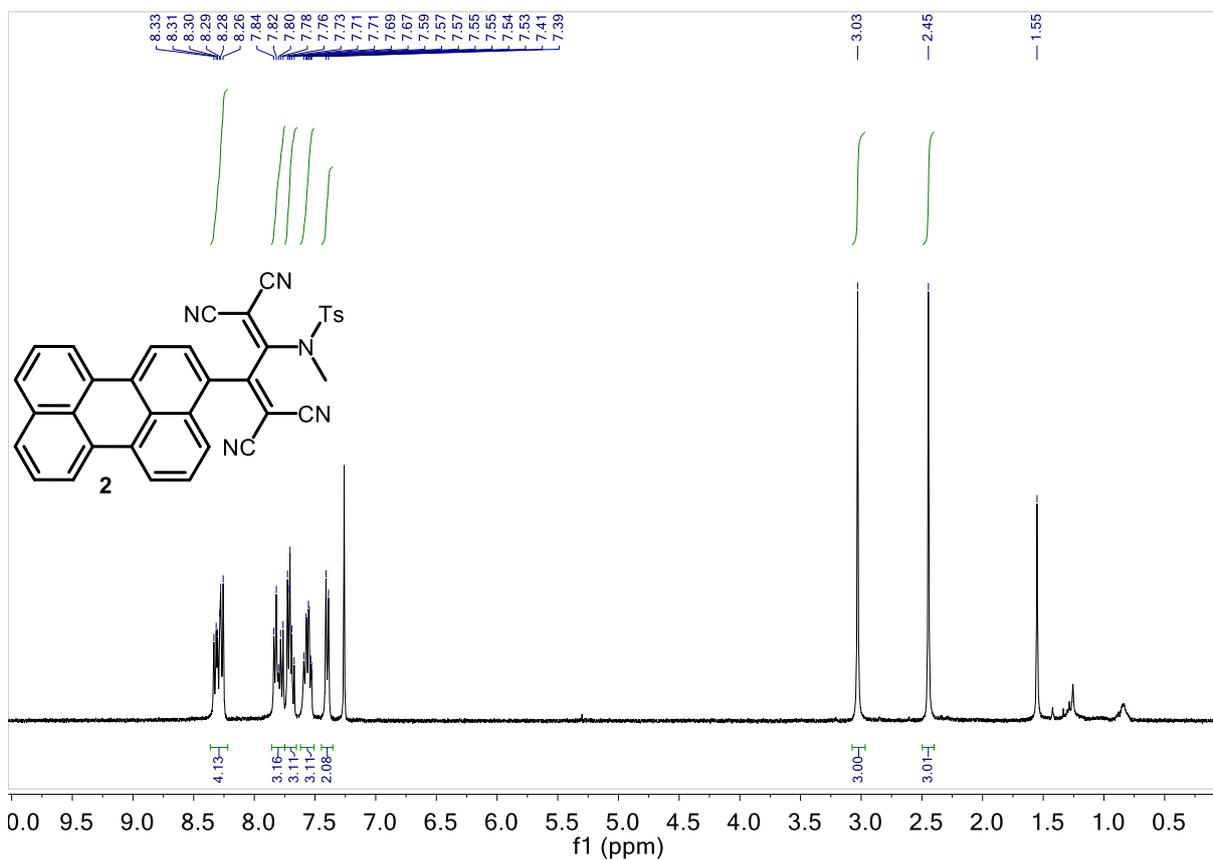


Figure S11. ^1H (300 MHz, CDCl_3) NMR spectrum of **2** recorded at 25°C.

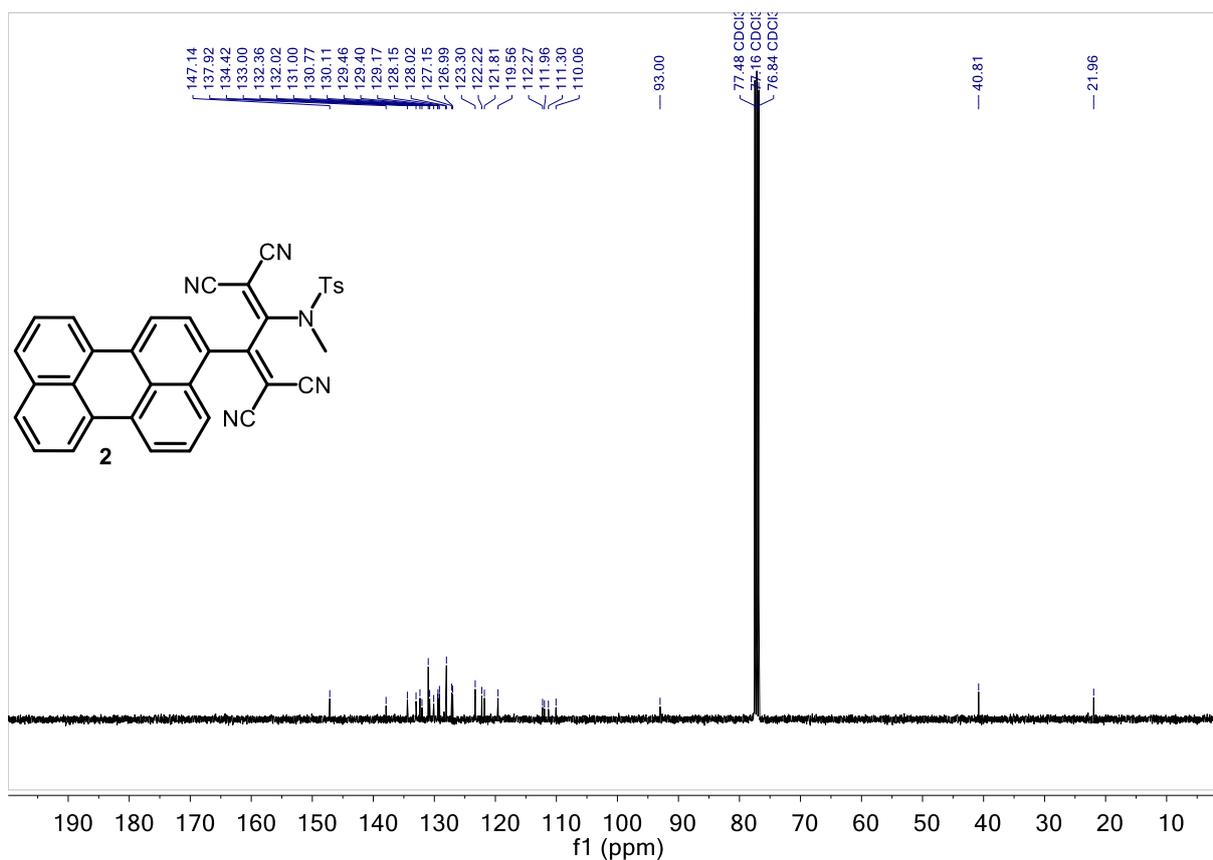
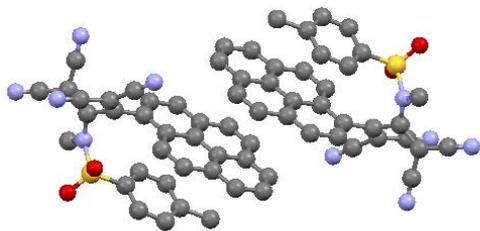


Figure S12. ^{13}C (75 MHz, CDCl_3) NMR spectrum of **2** recorded at 25°C.

4. Crystallographic data

(a)



(b)

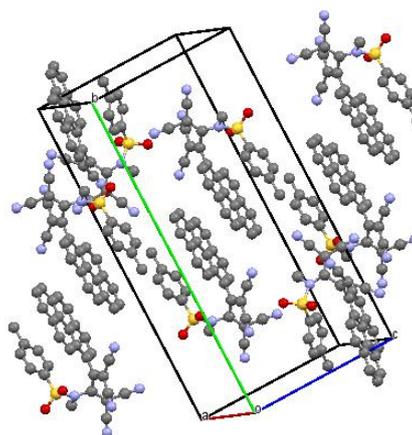


Figure S13. X-ray crystallographic structure of compound **1**: (a) discrete head-to-tail π -stacked dimer observed in the (b) crystal packing structure.

(a)

(b)

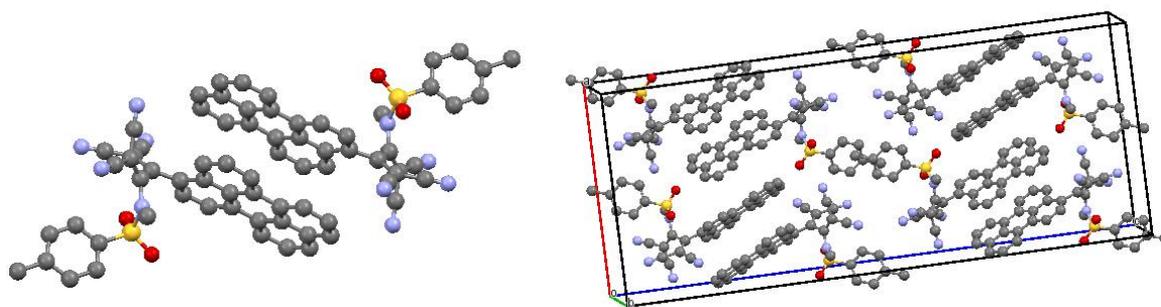
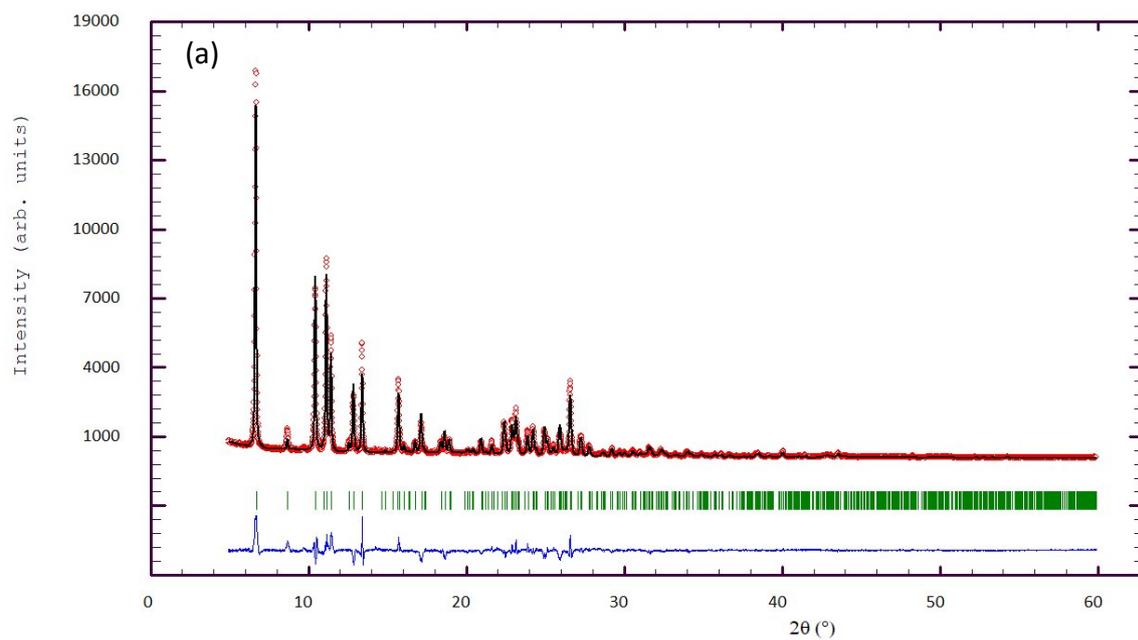
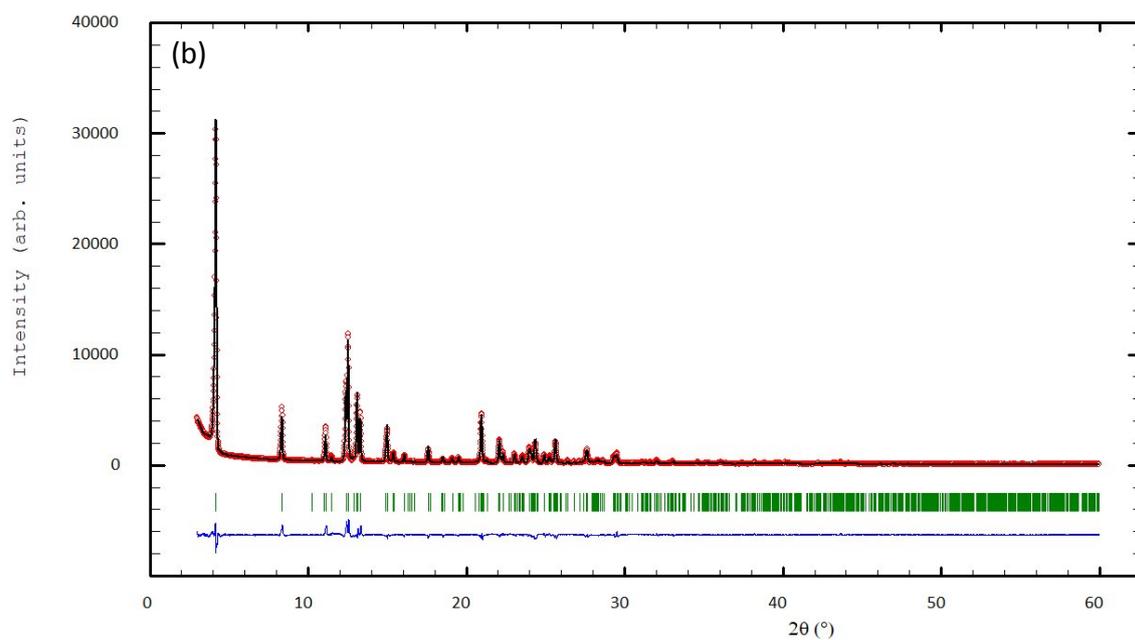


Figure S14. X-ray crystallographic structure of compound **2**: (a) discrete head-to-tail π -stacked dimer observed in the (b) crystal packing structure.



(a)



(b)

Figure S15. Rietveld-refined room-temperature powder X-ray diffraction patterns of the solid samples of (a) compound **1** and (b) compound **2**. Experimental (red open circles) and calculated data (black line) are displayed, along with the difference (blue line). The green ticks indicate the corresponding theoretical Bragg peak positions.

Table S1. Lattice parameters extracted from the Rietveld refinement of the room-temperature powder X-ray diffraction patterns

Compound	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å ³)
1	8.8291 (13)	26.3597 (43)	11.7038 (17)	90.0000	109.785 (11)	90.0000	2563.1 (7)
2	17.2764 (28)	7.8344 (14)	42.3447 (64)	90.0000	90.850 (14)	90.0000	5731 (2)

5. Photophysical data

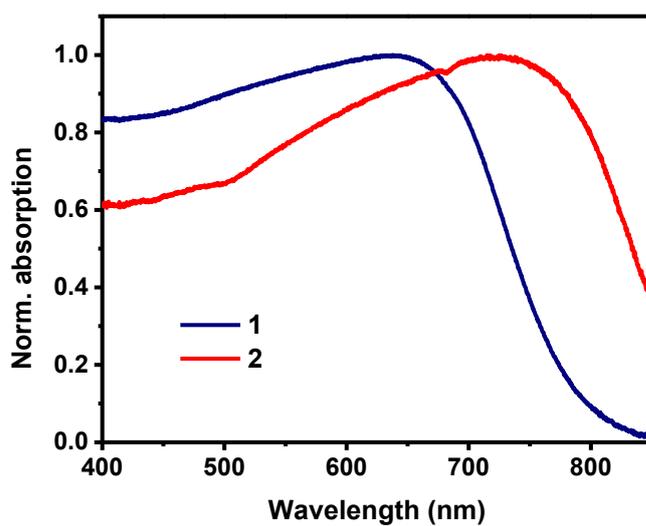


Figure S16. Normalized absorption spectra of compound **1** (dark blue) and **2** (red) in the solid state (powders).

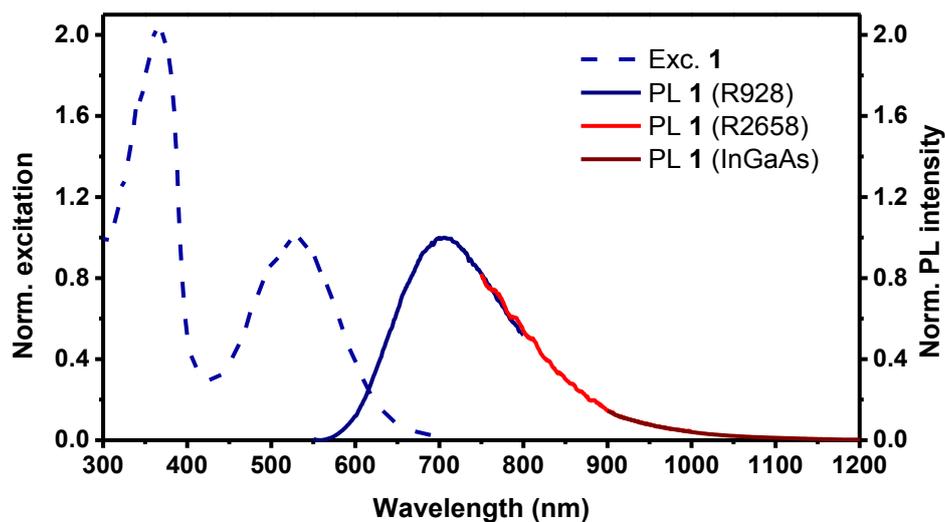


Figure S17. Normalized excitation (dashed line) and PL (solid line, $\lambda_{\text{exc}} = 530$ nm) spectra of compound **1** in MeTHF solvent glass at 77K (detectors: R928 PMT, R2658 PMT, InGaAs photodiode).

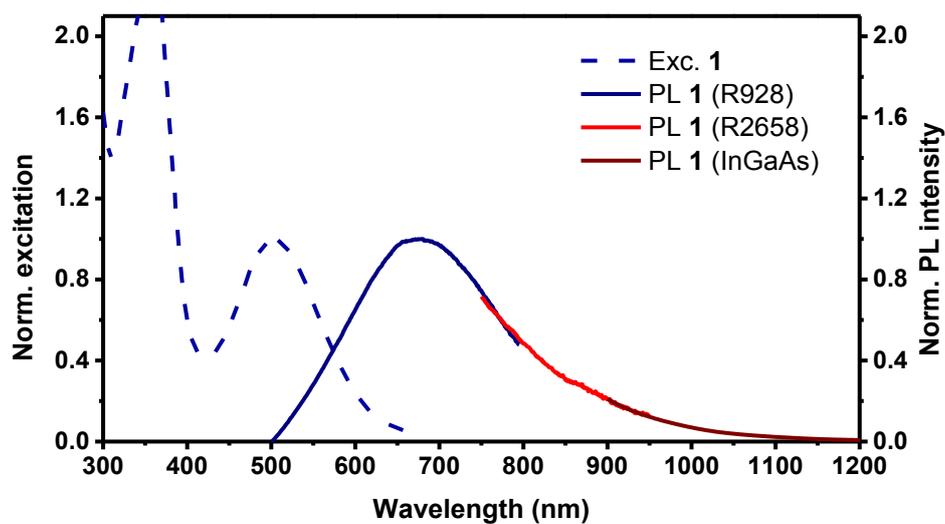


Figure S18. Normalized excitation (dashed line) and PL (solid line, $\lambda_{\text{exc}} = 480$ nm) spectra of compound **1** in PMMA matrix at room temperature (detectors: R928 PMT, R2658 PMT, InGaAs photodiode).